

Chemical Modification of Semiconductor Electrodes for the Photoelectrochemical
Splitting of Water

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Abstract

In the investigation of renewable energy technologies, one must consider inexpensive and efficient means of energy production and storage. Hydrogen can serve as both an energy storage mechanism and as a direct fuel to be used in fuel cells. Current technologies produce hydrogen from the reformation of fuels, or from the electrolysis of water using non-renewable energy sources. This paper looks at the renewable production of hydrogen from water, creating a closed, non-polluting cycle. The purpose of this research is to combine solar light collection and an electrolysis device into one monolithic device to attain the renewable and efficient splitting of water. In order to reach this goal, a semiconductor fitting criteria relating to band gap, band edge overlap, and charge transfer must be found. Using GaInP₂, we hoped to engineer the band edges and catalyze charge transfer through a series of surface modifications using organometallic compounds. Several different phthalocyanines with different metal and non-metal centers were studied, as well as two organic polymers; PTCDA and PDDA. None of the compounds studied showed a band edge shift in the direction needed to split water. The ability of these compounds to catalyze charge transfer was not studied, though their use as a catalyst cannot be ruled out.

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Introduction

As fossil fuel prices and pollution levels rise, renewable energy technologies are quickly being brought to attention. Possibilities for a future energy economy include power sources such as photovoltaics, wind, geothermal, hydroelectric, and biomass among others. Due to the intermittence of these energy resources (the sun does not always shine, the wind does not always blow), a viable energy storage and carrier system needs to be developed. Hydrogen fits our energy storage needs, and can provide clean electricity when used in a fuel cell, with water as the sole byproduct. Energy collected from renewable sources during non-peak usage can be turned into hydrogen for storage until the energy is at a greater demand.

Factors such as production, storage, and infrastructure determine the feasibility of a hydrogen economy. The focus of our research is on the renewable production of hydrogen. Hydrogen can be produced by fuel reforming, biomass conversion, and water electrolysis. Water electrolysis requires an input of energy to split water into hydrogen and oxygen. This energy input will ideally come from renewable energy, such as solar, wind, or hydropower. Systems that directly split water using sunlight are being investigated to minimize energy losses due to intermediate storage and conversion. This type of technology will allow the direct conversion of solar energy into hydrogen using semiconductor photoelectrochemistry.

The photoelectrochemical system used to convert sunlight into hydrogen consists of a semiconductor electrode in contact with an aqueous electrolyte solution. When the semiconductor is irradiated with light, the energy is enough to create electricity in the electrode, and thus split water into hydrogen and oxygen. For the direct photoelectrochemical

decomposition of water to occur, several key criteria of the semiconductor must be met. The semiconductor's band gap must be sufficient enough to split water ($\sim 1.7\text{eV}$), the band edges of the semiconductor and that of water must overlap, and finally the charge transfer from the surface of the semiconductor must be fast enough to prevent corrosion and band edge shift. Gallium indium phosphide, the semiconductor used in this research, has a band gap of $1.8 - 1.9\text{eV}$, thus meeting the first of the criteria. Its band edges are shifted, however, and do not overlap that of water. The electrode also accumulates charge at its surface, thus contributing to surface corrosion and further band edge shift away from the desired potentials.

Surface modification of the semiconductor electrode can help the system meet the above criteria. By etching the electrode and performing different surface treatments, the band edges can be shifted and charge transfer catalyzed. Previous research has shown that organic molecules shift the band edges of the semiconductor, and transition metals catalyze charge transfer from its surface. This research combines these concepts by investigating the effect of organometallic compounds on the band edge position and charge transfer at the surface of gallium indium phosphide semiconductors.

Materials and Methods

Semiconductor Electrodes

Our research focuses on gallium indium phosphide semiconductors. Gallium indium phosphide is a p-type semiconductor, using holes as the main source of charge transfer. It has a band gap of approximately 1.83 eV , slightly more than that needed to split water. The semiconductor samples are prepared by a group at the National Renewable Energy Lab, and are

grown by metalorganic vapor phase deposition on gallium arsenide substrates. Electrodes were prepared from approximately 0.1 cm² pieces of semiconductor, attached to coiled copper wire with silver paint. The body of the wire was encased in glass tubing, and a layer of non-conducting epoxy used to seal the electrode and expose only the semiconductor surface to the solution.

All electrodes were etched prior to use to remove surface oxides on the semiconductor surface. The electrodes were immersed in concentrated sulfuric acid for 10-15 seconds, then rinsed with de-ionized water. The electrode was then dried under nitrogen and immediately placed in the sample cell. If the electrode had been previously treated with a phthalocyanine compound, it was first rinsed with dichloroethane to remove any adsorbed organics.

Chemicals

Solutions of chemicals were made based on solubility using pH 7 buffer, pH 0 potassium sulfate, pH 12 buffer, and dichloroethane as solvents. All chemicals used were reagent grade. For the drop coating experiments, one drop of a 0.1mM DCE/phthalocyanine solution was placed on an etched semiconductor surface, evaporated under dry nitrogen, and immediately placed in the sample cell. For the electrolyte experiments, the electrolyte in the sample cell was a 0.1mM phthalocyanine solution in either pH 7, pH 0, or pH 12 buffer.

Electrochemical Analysis

The cell set-up consisted of the working electrode previously described, a platinum mesh counter electrode, and a saturated calomel reference electrode, all immersed in an electrolyte

solution. A Solartron impedance analyzer was used to perform the electrochemical measurements.

Baseline electrochemical measurements were taken to determine the flat-band potentials of our untreated semiconductors. The semiconductor was etched in sulfuric acid, and then placed in the sample cell with either pH 7, pH 0, or pH 12 solution. A Mott-Schottky analysis was run and the data used to determine the flat-band potential of the untreated semiconductor.

Once these baseline measurements were achieved, one set of data was obtained with different surface treatments on the electrode. A drop of a metal-phthalocyanine solution was placed on the surface of the etched semiconductor, and the solvent evaporated to leave a film on the semiconductor surface. This electrode was then placed in the sample cell and run in the same buffer solutions previously mentioned. Other electrochemical measurements were obtained by varying the electrolyte solution in the sample cell. The etched, untreated electrode was placed in the sample cell, which contained a solution of a metal-phthalocyanine in pH 7 buffer. A Mott-Schottky analysis of electrochemical data was run, and the shift in the flat-band potentials from the baseline measurements was determined. If the compound was determined to cause a significant shift in the flat-band potential, then it was further investigated in different pH conditions.

Results

The flat-band potentials of etched, untreated semiconductor electrodes were measured to achieve a consistent baseline reading. The average flat-band potentials of untreated electrodes with standard deviations are listed in Table 1. The flat-band potentials of electrodes treated with different phthalocyanines and PDDA and PTCDA in pH 7 buffer can be seen relative to baseline

readings in Figures 1 and 2. Further studies on molecules of interest were done in pH 12 and pH 0 buffers as well, seen in Figures 3 and 4 respectively.

Discussion

None of the phthalocyanines or other molecules tested resulted in a significant positive shift in the flat-band potentials of the semiconductor. Light studies on these molecules were not performed, since the criteria of band edge shift was not met. However, this does not rule these compounds out as charge transfer catalysts. Further studies can be done to determine their effectiveness as catalysts alone, without meeting band edge shift criteria.

Acknowledgements

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Tables

Baseline Measurements (V)		
pH	Average	S.D.
0	0.57	0.05
7	0.33	0.04
12	0.08	0.006

Table 1. Average flat-band potentials of untreated electrodes taken as baseline measurements.

Figures

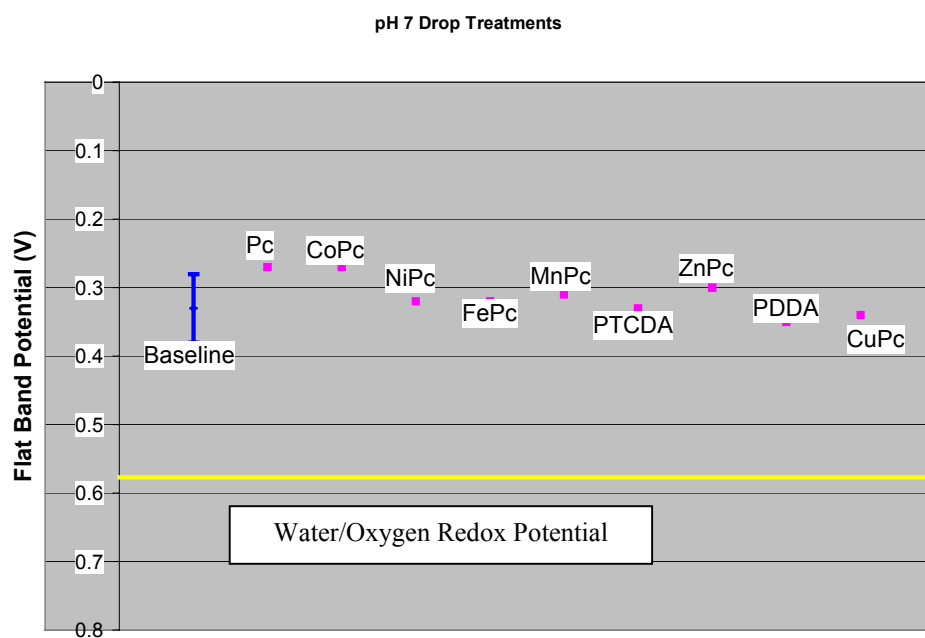


Figure 1. Flat-band potentials of electrodes drop treated with various compounds run in pH 7 buffer.

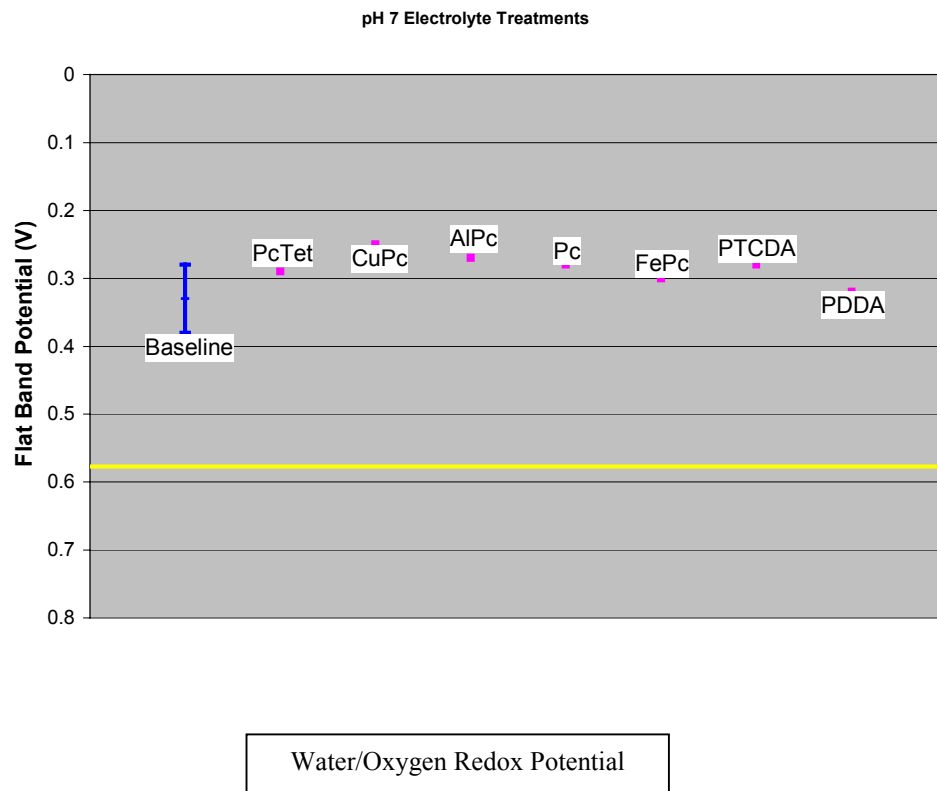


Figure 2. Flat-band potentials of electrodes run in various pH 7 electrolyte solutions.

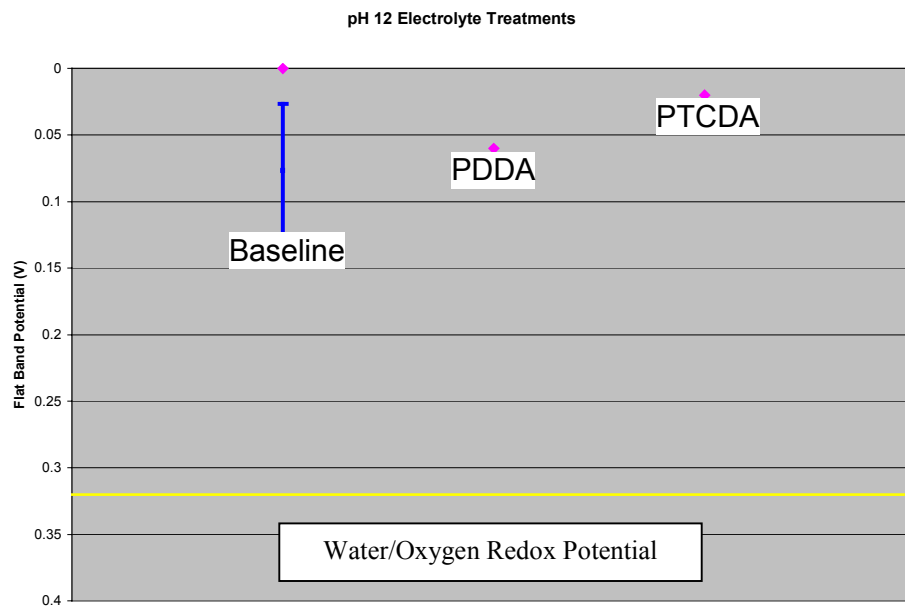


Figure 3. Flat-band potentials of electrodes run in various pH 12 electrolyte solutions.

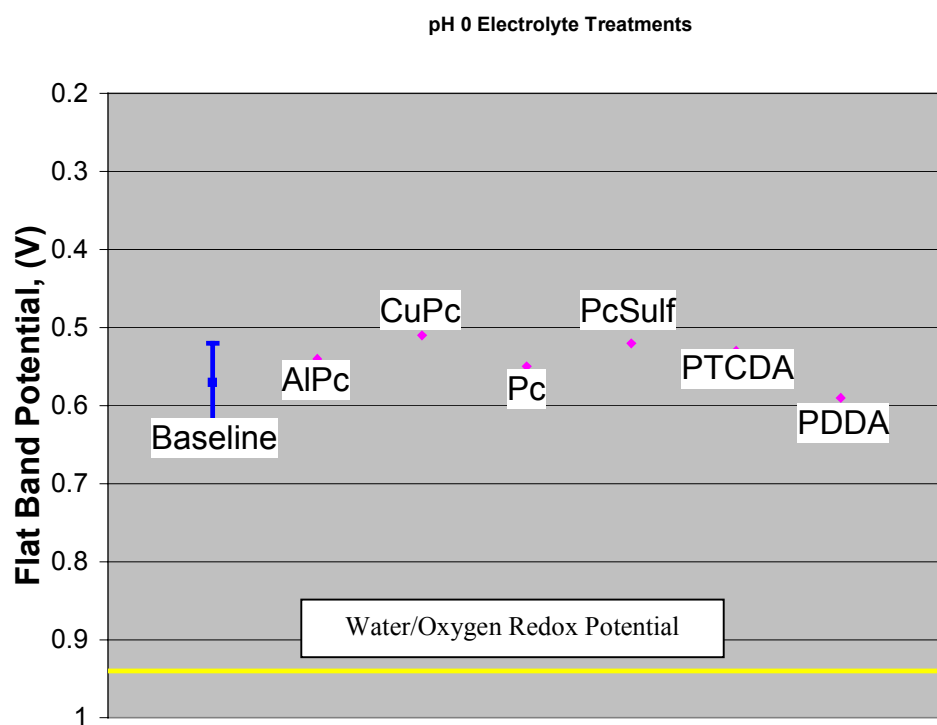


Figure 4. Flat-band potentials of electrodes run in various pH 0 electrolyte solutions.